

Film-forming coating agents

Publication number: GB901709

Publication date: 1962-07-25

Inventor:

Applicant: HENKEL & CIE GMBH

Classification:

- international: **A61K8/04; A61K8/81; A61Q5/06; C09D133/26; C11D17/00; A61K8/04; A61K8/72; A61Q5/06; C09D133/24; C11D17/00;**

- European: A61K8/04F; A61K8/81K6; A61Q5/06; C09D133/26; C11D17/00D

Application number: GB19610009752 19610317

Priority number(s): DE1960H039372 19600507

Also published as:



NL263645 (A)

CH467811 (A5)

BE601265 (A)

DE1169064 (B1)

[Report a data error here](#)

Abstract of GB901709

Articles are coated with a film-forming agent comprising a solution in an aliphatic alcohol and/or water of a copolymer of acrylamide and one or more N-alkylacrylamides containing 1 or 2 alkyl groups containing a total of 2 to 6 carbon atoms, especially N-tert.-butylacrylamide. The following applications are described: (1) a solution of the copolymer, e.g. in ethanol, is applied to a metal body, e.g. an iron sheet, a machine part or a complete car, the solution containing, if desired, corrosion inhibitors such as dicyclohexylammonium nitrite, sodium benzoate, thiourea and substituted thioureas, the resulting coating being removable with aqueous detergent solutions; and (2) tablets of washing agents are coated with an alcoholic solution of the copolymer, an exemplified washing agent consisting of tetrapropylbenzene sulphonate, soap, the addition product of ethylene oxide and nonyl phenol, carboxymethyl cellulose, perborate, sodium tripolyphosphate, waterglass, sodium sulphate and water. ALSO: A film-forming coating agent comprises a solution in an aliphatic alcohol and/or water of a copolymer of acrylamide and one or more N-alkylacrylamides containing 1 or 2 alkyl groups containing a total of 2 to 6 carbon atoms, especially N-tert.-butylacrylamide. Aliphatic alcohols specified are ethanol and isopropanol. The coating agents may be applied in the following ways: (1) a solution of the copolymer in an alcohol is dissolved in a halogenated hydrocarbon, e.g. methylene chloride or a fluorochlorohydrocarbon, and packed in an aerosol spray capsule for use as a hair fixative; (2) an alcoholic solution of the copolymer is used to coat hygroscopic substances, e.g. washing agents; (3) a solution of the copolymer, e.g. in ethanol, is applied to a metal, e.g. steel, surface, the solution containing, if desired, corrosion inhibitors such as dicyclohexylammonium nitrite, thiourea or substituted thioureas and sodium benzoate; and (4) an aqueous solution of the copolymer is used to coat tablets of nigrosin. ALSO: Tablets of alcohol-soluble dyestuffs, e.g. nigrosin, are coated with a film-forming agent comprising an aqueous solution of a copolymer of acrylamide and one or more N-alkylacrylamides containing 1 or 2 alkyl groups which contain a total of 2 to 6 carbon atoms, especially N-tert.-butylacrylamide. ALSO: An aerosol spray hair fixative composition comprises an alcoholic solution of a copolymer of acrylamide and one or more N-alkyl substituted acrylamides containing 1 or 2 alkyl groups containing a total of 2 to 6 carbon atoms, e.g. N-tert.-butylacrylamide, together with a halogenated hydrocarbon, e.g. methylene chloride and dichlorodifluoromethane. Isopropanol is specified as a suitable solvent for the copolymer.

Data supplied from the **esp@cenet** database - Worldwide

PATENT SPECIFICATION

NO DRAWINGS

901,709



Date of Application and filing Complete Specification :
March 17, 1961.

No. 9752/61.

Application made in Germany (No. 39,372) on May 7, 1960.

Complete Specification Published July 25, 1962.

Index at Acceptance: Classes 2(6), P8A, P8C(12A:14A:14B:16A:16C:17:18:20B),
P8(D4:K8); 15(2), J; 81(1), L4; 91, D2(F:G:N:P:Q:V:X), S2(F:G:N:P:Q:V), S11; and 95, B4X.
International Classification: C08f. A61k. B05. C09b. C11d.

Film-forming coating agents.

COMPLETE SPECIFICATION

We, HENKEL & Cie G.m.b.H. a Germany Company, of 67, Henkelstrasse, Duesseldorf-Holthausen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to film-forming coating agents, particularly to such agents which are stable to moisture, and which form clear and colourless coatings.

It is known to use co-polymers from esters of unsaturated carboxylic acids and N-substituted acrylic acid amides, the ester groups of which have been saponified after the polymerisation, as a hair fixative and a covering agent for skin spots. Apart from the expensive 2-stage method of preparation the film produced with these products have not a clear appearance and only little strength. Furthermore, they are hygroscopic and therefore soften in a moist atmosphere.

It has now been surprisingly found that co-polymers from unsubstituted acrylamide and N-substituted acrylamides prepared by known methods do not have the said disadvantages and display good film-forming properties, above all when the alkyl residues of the N-alkylacrylamide contain 2 to 6 carbon atoms.

Accordingly this invention provides a film forming coating agent comprising a solution in a lower aliphatic alcohol and/or water of a copolymer from acrylamide and N-alkylacrylamide, in which the alkyl group comprises 1 or 2 lower alkyl groups containing a total of carbon atoms lying the range 2 to 6.

The co-polymers according to the invention are suitable for the production of coatings. They form clear, almost colourless films of good coherence and which have no components of a "crystalline" appearance i.e. the films do not become scaly. The

films are non-hygroscopic and scarcely soften even in a moist atmosphere.

Nevertheless, the films produced from the co-polymers according to the invention show a sufficient solubility in water or, in the case of higher fractions of substituted acrylamides such as *tert*-butylacrylamide, a good emulsifiability in water, so that the coatings are easily removable.

A further advantage of the products used according to the invention is the miscibility of their solutions in lower aliphatic alcohols with halogenated hydrocarbons, which are used as aerosol spray propellants, e.g. methylene chloride and lower fluorochloro-hydrocarbons. This miscibility makes possible the use of these solutions in aerosol spray capsules. In the preparation of the alcoholic solutions for this purpose, it may be observed that small amounts of water are usually added in order to obtain a homogeneous solution of the copolymer in ethyl alcohol or isopropyl alcohol. Only just sufficient water to obtain a good solubility should be added, however, in order that on mixing with the propellant for the spray capsule separation of water does not take place.

When the copolymers are used as hair fixatives, additives known for this purpose may also be incorporated such as perhaps perfume and small amounts of surface-active substances. The addition of water-repelling additives is unnecessary in most cases. Copolymers from acrylamide and *N-tert*. butylacrylamide in which the proportions by weight are between 1:7 and 1:8 are especially suitable for use as hair fixatives which are employed in aerosol spray capsules. These in fact are not dissolved in pure water, but may be removed from the hair easily and completely by means of the usual hair shampoos.

In addition, the copolymers according to the invention may be used as coating agents

for metals, e.g. machine parts, in order to prevent corrosion and contamination. Products prepared from acrylamide and *N-tert.* butylacrylamide, in which the proportions by weight of the starting substances are 1:7 to 1:8 are also particularly suitable for the above purpose. The machine parts coated with a film of the copolymers just mentioned may be stored for a long time. Immediately before their use, the film may be removed by known aqueous solutions of cleaning agents such as, say, dodecylbenzenesulphonate. Obviously the film-forming solutions may be admixed with known corrosion inhibitors for example dicyclohexylammonium nitrite, sodium benzoate, thiourea and substituted thioureas. In this way separate machine parts or, for example, complete cars may be enveloped, the stability of the copolymers containing a high percentage composition of substituted acrylamide, making possible the safe storage thereof, free from water even when the composite is in the open.

Furthermore, hygroscopic substances may be coated with a thin film of the copolymers, according to the invention, in order to protect them from the effects of a damp atmosphere. Thus tablets of washing agents which have been impregnated by immersing in an alcoholic solution of the copolymers may be kept for a long time in damp rooms, such as perhaps in the bathroom, without becoming sticky or unsightly.

By virtue of the solubility in alcohol and water of the copolymers which contain about equal parts of acrylamide and substituted acrylamide, tablets of alcohol-soluble dyestuffs may also be coated by immersing in aqueous solutions of the copolymers. By this means good cohesion of the tablets is attained and powdering of the dyestuff is prevented. On throwing into alcohol the coating and the tablet itself dissolve on stirring.

The invention will now be further described by way of Examples.

EXAMPLE 1

A solution of 15 g of acrylamide and 0.09 g of sodium pyrosulphite in 220 c.c. of water and a solution of 30 g of *N-tert.* butylacrylamide in 165 c.c. of acetone are united and polymerised by addition of 0.09 g of ammonium persulphate in 20 c.c. of water at 40°C over a period of three hours. After the reaction was completed, a light-coloured powder with a K value of 84 was obtained by drum drying. 16 g of the dry product were suspended by stirring in 170 c.c. of isopropanol and 14 c.c. of water were added thereto. After a short time a homogeneous highly viscous solution was formed.

4 g of this solution together with 35.5 g of alcohol with addition of 0.5 g of perfume were filled with 60 g of dichlorodifluoro-

methane into an aerosol spray capsule. This solution was suitable as a hair spray, for example, and on spraying provided a water-soluble clear film of excellent coherence. Even in a damp atmosphere this film was not unsightly and sticky. On the other hand, it could be removed easily with water.

EXAMPLE 2

A solution of 18 g of acrylamide and 0.05 g of sodium pyrosulphite in 120 c.c. of water was heated to 40°C and united with a solution of 72 g of *N-tert.* butylacrylamide in 680 c.c. of acetone saturated with nitrogen. After heating to 40°C the polymerisation was initiated by addition of 0.09 g of ammonium persulphate in 10 c.c. of water. After a short time the temperature rose to 44°C. The reaction vessel was allowed to stand overnight in a water bath at 40°C and the polymer was then precipitated by pouring the solution into a large quantity of water. After drying, 81 g, corresponding to 90% of theory, of a white product which had a K-value of 94 were obtained.

The reaction product was soluble in isopropanol without any addition of water. The solution could be blended with halogenated hydrocarbons. A 0.8% solution in isopropanol was filled into an aerosol spray capsule with addition of dichlorodifluoromethane. On spraying a clear water-insoluble film was formed, which was quickly and completely soluble in dilute solutions of the usual washing agents. By virtue of these properties the mixture described could be used with advantage as a hair fixative.

EXAMPLE 3

15 g of acrylamide and 15 g of *N-tert.* butylacrylamide were dissolved in a mixture of 165 c.c. of water and 50 g of acetone and treated at 60°C with a solution of 0.025 g of potassium persulphate in 30 c.c. of water. After polymerising for two hours, a light, light-coloured powder was obtained by drying the solution obtained on a heated drum.

20 g of this product were dissolved in 250 c.c. of 90% ethanol. Tablets of washing agents 50 g in weight of the composition given below were immersed in the solution and dried in the air.

According to a preferred form of the invention, the substituent on the nitrogen is a *tert.*-butyl group and the proportion by weight of acrylamide to *N-tert.*-butylacrylamide in the preferred polymer lies in the range 5.5 : 4.5 to 1 : 8.5.

The following, for example, may be used as substituents: *n*-propyl, *isopropyl*, *n*-butyl, *isobutyl*, *tert.*-butyl, *n*-pentyl, *isopentyl*, *neopentyl*. The substituted acrylamide may also carry 2 substituents on the nitrogen, while the total number of carbon atoms in these substituents preferably amounts to 2-6,

e.g. 2 ethyl or one methyl and one propyl group. The co-polymers to be used according to the invention may in addition contain several of the said *N*-substituted acrylamides.

5 The ratio of unsubstituted to substituted acrylamide in the co-polymers depends upon the use intended and the constitution of the substituted acrylamide. By simple experiments it is possible to prepare readily a product having the requisite solubility and other properties desired for the particular application envisaged. As mentioned earlier the co-polymers from acrylamide and *N*-*tert*-butylacrylamide, in which the proportion by weight of unsubstituted to substituted acrylamide lies between 5.5 : 4.5 to 1 : 8.5, have especially favourable film-forming properties

Tablet mixture	
20 Tetrapropylbenzenesulphonate	5%
Perborate	20%
Addition product of ethylene oxide to nonylphenol	2%
Soap	10%
Sodium tripolyphosphate	45%
25 Carboxymethylcellulose	1%
Waterglass	1%
Sodium sulphate	11%
Water	5%
30 These tablets coated with a film of the copolymer from equal parts of acrylamide and <i>N</i> - <i>tert</i> -butylacrylamide remained dry and of pleasing appearance even after storage for 10 weeks in a damp atmosphere at 30°C. On throwing into slightly moving water the tablets dissolved.	

EXAMPLE 4

A solution of 30 g of acrylamide and 70 g of *N*-*tert*-butylacrylamide in 650 c.c. of water and 300 g of acetone was copolymerised in the usual way at 40°C by addition of 0.1 g of sodium pyrosulphite and 1.3 g of ammonium persulphate, and, after 6 hours on a heated band, the solution obtained dried to a loose light-coloured powder. With addition of 5% of thiourea, based on the copolymer, a 4% solution of the reaction product in 95% ethanol was prepared.

50 Iron sheets 4 x 12 cm in size were immersed in the solution and dried in the air. The sheets were kept for 12 weeks at 25°C in a damp atmosphere. After this time the sheets were bright. The film of the copolymer was washed off with a 1%

solution at 40°C of a commercial alkylbenzenesulphonate, this being possible without difficulty.

EXAMPLE 5

A 4% aqueous solution was prepared from a copolymer from equal parts of acrylamide and *N*-*tert*-butylacrylamide. With it were coated by immersion, pressed tablets from an alcohol-soluble dyestuff which is commercially available as "Nigrosin soluble in spirit" (ch. G. Schultz, Farbstofftabellen, 1931, p. 427). The tablets so obtained did not powder and dissolved well in alcohol.

WHAT WE CLAIM IS:

1. A film-forming coating agent comprising a solution in an aliphatic alcohol and/or water of a copolymer from acrylamide and *N*-alkylacrylamide, in which the alkyl group comprises 1 or 2 alkyl groups containing a total of carbon atoms lying in the range 2 to 6.

2. A film-forming coating agent, as claimed in claim 1, in which the alkyl residue is an *N*-*tert*-butyl residue.

3. A film-forming coating agent as claimed in claim 2 in which the proportion by weight of acrylamide to *N*-*tert*-butylacrylamide lies between 5.5 : 4.5 to 1 : 8.5.

4. A film-forming coating agent as claimed in any of claims 1 to 3, in which said solution also contains an aerosol spray propellant.

5. A film-forming coating agent as claimed in claim 4 in which said aerosol spray propellant is a volatile fluorochlorohydrocarbon.

6. A film coating agent as claimed in claim 1, substantially as described herein with particular reference to Example 1.

7. A film coating agent as claimed in claim 1, substantially as described herein with particular reference to Examples 2 to 5.

8. A method of preparing a film-coated surface or article comprising the application to the surface or article of a film coating agent as claimed in any of the preceding claims.

9. A method as claimed in claim 8 in which said application is carried out by means of a spray.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1.
Chartered Patent Agents.